Table S24. Selected bond lengths [Å] and angles [°] for tBuSpTa(CH_2CHPh)H (22, CCDC 142045).

Ta-Cent(1)	2.068(5)	Cent(1)-Ta-Cent(2)	131.94(1)
Ta-Cent(2)	2.084(5)	Pln(1)-Ta-Pln(2)	125.2(3)
Ta-Pln(1)	2.081(3)		
Ta-Pln(2)	2.062(3)		

Table S25. Bond lengths [Å] and angles [°] for tBuSpTa(CH_2CHPh)H (22, CCDC 142045).

Ta-Cent(1)	2.068(5)	C(14)-H(14C)	1.0447
Ta-Cent(2)	2.084(5)	C(15)-H(15A)	0.9807
Ta-Pln(1)	2.081(3)	C(15)-H(15B)	0.9807
Ta-Pln(2)	2.062(3)	C(15)-H(15C)	0.9807
Ta-C(17)	2.267(9)	C(16)-H(16A)	0.7188
Ta-C(18)	2.307(7)	C(16)-H(16B)	0.7188
Ta-C(6)	2.334(5)	C(16)-H(16C)	0.7188
Ta-C(1)	2.359(6)	C(17)-C(18)	1.445(9)
Ta-C(10)	2.358(5)	C(17)-H(17A)	0.9739
Ta-C(7)	2.367(7)	C(17)-H(17B)	0.9739
Ta-C(2)	2.381(8)	C(18)-C(19)	1.483(7)
Ta-C(5)	2.375(7)	C(18)-H(18)	0.7398
Ta-C(4)	2.419(7)	C(19)-C(20)	1.384(12)
Ta-C(9)	2.449(6)	C(19)-C(24)	1.381(10)
Ta-C(3)	2.466(6)	C(20)-C(21)	1.398(8)
Ta-C(8)	2.476(7)	C(20)-H(20)	0.9300
Ta-H	1.8669	C(21)-C(22)	1.377(12)
Si-C(6)	1.858(7)	C(21)-H(21)	0.8784
Si-C(11)	1.856(9)	C(22)-C(23)	1.361(13)
Si-C(12)	1.850(8)	C(22)-H(22)	1.0306
Si-C(1)	1.876(6)	C(23)-C(24)	1.380(8)
C(1)-C(5)	1.409(12)	C(23)-H(23)	0.7862
C(1)-C(2)	1.429(9)	C(24)-H(24)	0.8519
C(2)-C(3)	1.401(10)		
C(2)-H(2)	0.8711	Cent(1)-Ta-Cent(2)	131.94(1)
C(3)-C(4)	1.387(12)	Pln(1)-Ta-Pln(2)	125.2(3)
C(3)-H(3)	1.0994	C(17)-Ta-C(18)	36.8(2)
C(4)-C(5)	1.380(8)	C(17)-Ta-C(6)	113.8(2)
C(4)-H(4)	0.9300	C(18)-Ta-C(6)	136.9(2)
C(5)-H(5)	0.9978	C(17)-Ta-C(1)	114.8(3)
C(6)-C(10)	1.421(11)	C(18)-Ta-C(1)	140.5(3)
C(6)-C(7)	1.433(10)	C(6)-Ta-C(1)	70.7(2)
C(7)-C(8)	1.434(9)	C(17)-Ta-C(10)	81.0(2)
C(7)-H(7)	1.0524	C(18)-Ta-C(10)	102.3(2)
C(8)-C(9)	1.398(12)	C(6)-Ta-C(10)	35.2(3)
C(8)-C(13)	1.510(9)	C(1)-Ta-C(10)	95.5(2)
C(9)-C(10)	1.442(8)	C(17)-Ta-C(7)	135.6(2)
C(9)-H(9)	0.7546	C(18)-Ta-C(7)	131.9(2)
C(10)-H(10)	0.9396	C(6)-Ta-C(7)	35.5(2)
C(11)-H(11A)	0.9312	C(1)-Ta-C(7)	87.4(2)
C(11)-H(11B)	0.9312	C(10)-Ta-C(7)	57.9(3)
C(11)-H(11C)	0.9312	C(17)-Ta-C(2)	135.4(3)
C(12)-H(12A)	0.9587	C(18)-Ta-C(2)	134.3(2)
C(12)-H(12B)	0.9587	C(6)-Ta-C(2)	88.6(2)
C(12)-H(12C)	0.9587	C(1)-Ta-C(2)	35.1(2)
C(13)-C(16)	1.528(9)	C(10)-Ta-C(2)	122.2(2)
C(13)-C(14)	1.519(11)	C(7)-Ta-C(2)	85.0(3)
C(13)-C(15)	1.538(10)	C(17)-Ta-C(5)	82.3(3)
C(14)-H(14A)	1.0447	C(18)-Ta-C(5)	106.4(3)
C(14)-H(14B)	1.0447	C(6)-Ta-C(5)	94.1(2)

C(1)-Ta-C(5)	34.6(3)	C(6)-Si-C(11)	110.0(4)
C(10)-Ta-C(5)	102.7(2)	C(6)-Si-C(12)	113.3(4)
C(7)-Ta-C(5)	120.1(2)	C(11)-Si-C(12)	113.1(4)
C(2)-Ta-C(5)	57.0(3)	C(6)-Si-C(1)	93.2(3)
C(17)-Ta-C(4)	80.4(3)	C(11)-Si-C(1)	113.6(3)
C(18)-Ta-C(4)	86.5(3)	C(12)-Si-C(1)	112.1(3)
C(6)-Ta-C(4)	125.7(2)	C(5)-C(1)-C(2)	106.2(5)
C(1)-Ta-C(4)	56.6(2)	C(5)-C(1)-Si	124.3(5)
C(10)-Ta-C(4)	134.3(2)	C(2)-C(1)-Si	123.6(6)
C(7)-Ta-C(4)	140.0(3)	C(5)-C(1)-Ta	73.3(4)
C(2)-Ta-C(4)	55.8(3)	C(2)-C(1)-Ta	73.3(4)
C(5)-Ta-C(4)	33.45(19)	Si-C(1)-Ta	97.0(3)
C(17)-Ta-C(9)	80.4(3)	C(3)-C(2)-C(1)	108.2(8)
C(18)-Ta-C(9)	82.1(2)	C(3)-C(2)-Ta	76.6(5)
C(6)-Ta-C(9)	58.0(2)	C(1)-C(2)-Ta	71.6(4)
C(1)-Ta-C(9)	127.74(19)	C(3)-C(2)-H(2)	125.9
C(10)-Ta-C(9)	34.9(2)	C(1)-C(2)-H(2)	125.9
C(7)-Ta-C(9)	56.5(3)	Ta-C(2)-H(2)	117.8
C(2)-Ta-C(9)	141.2(3)	C(4)-C(3)-C(2)	107.4(6)
C(5)-Ta-C(9)	136.2(2)	C(4)-C(3)-Ta	71.6(4)
C(4)-Ta-C(9)	159.7(3)	C(2)-C(3)-Ta	69.9(4)
C(17)-Ta-C(3)	109.7(3)	C(4)-C(3)-H(3)	126.3
C(18)-Ta-C(3)	100.9(2)	C(2)-C(3)-H(3)	126.3
C(6)-Ta-C(3)	121.8(2)	Ta-C(3)-H(3)	123.8
C(1)-Ta-C(3)	56.68(19)	C(3)-C(4)-C(5)	109.5(7)
C(10)-Ta-C(3)	152.2(2)	C(3)-C(4)-Ta	75.4(4)
C(7)-Ta-C(3)	114.6(3)	C(5)-C(4)-Ta	71.5(4)
C(2)-Ta-C(3)	33.5(2)	C(3)-C(4)-H(4)	125.2
C(5)-Ta-C(3)	55.6(3)	C(5)-C(4)-H(4)	125.2
C(4)-Ta-C(3)	33.0(3)	Ta-C(4)-H(4)	119.5
C(9)-Ta-C(3)	166.8(3)	C(1)-C(5)-C(4)	108.5(7)
C(17)-Ta-C(8)	110.2(3)	C(1)-C(5)-Ta	72.1(4)
C(18)-Ta-C(8)	97.6(2)	C(4)-C(5)-Ta	75.0(4)
C(6)-Ta-C(8)	58.0(2)	C(1)-C(5)-H(5)	125.7
C(1)-Ta-C(8)	121.6(2)	C(4)-C(5)-H(5)	125.7
C(10)-Ta-C(8)	57.0(2)	Ta-C(5)-H(5)	119.0
C(7)-Ta-C(8)	34.4(2)	C(10)-C(6)-C(7)	106.7(6)
C(2)-Ta-C(8)	114.3(3)	C(10)-C(6)-Si	127.0(6)
C(5)-Ta-C(8)	151.91(19)	C(7)-C(6)-Si	121.2(6)
C(4)-Ta-C(8)	167.0(3)	C(10)-C(6)-Ta	73.3(3)
C(9)-Ta-C(8)	33.0(3)	C(7)-C(6)-Ta	73.5(3)
C(3)-Ta-C(8)	134.1(3)	Si-C(6)-Ta	98.4(3)
C(17)-Ta-H	112.4	C(6)-C(7)-C(8)	109.1(7)
C(18)-Ta-H	76.3	C(6)-C(7)-Ta	71.0(4)
C(6)-Ta-H	125.4	C(8)-C(7)-Ta	77.0(4)
C(1)-Ta-H	113.1	C(6)-C(7)-H(7)	125.5
C(10)-Ta-H	136.5	C(8)-C(7)-H(7)	125.5
C(7)-Ta-H	90.2	Ta-C(7)-H(7)	118.4
C(2)-Ta-H	78.1	C(9)-C(8)-C(7)	107.3(6)
C(5)-Ta-H	119.6	C(9)-C(8)-C(13)	127.0(7)
C(4)-Ta-H	89.2	C(7)-C(8)-C(13)	124.5(8)
C(9)-Ta-H	104.2	C(9)-C(8)-Ta	72.4(4)
C(3)-Ta-H	64.5	C(7)-C(8)-Ta	68.7(4)
C(8)-Ta-H	79.9	C(13)-C(8)-Ta	133.6(3)

C(8)-C(9)-C(10)	108.7(7)	C(13)-C(15)-H(15C)	109.5
C(8)-C(9)-Ta	74.6(4)	H(15A)-C(15)-H(15C)	109.5
C(10)-C(9)-Ta	69.1(3)	H(15B)-C(15)-H(15C)	109.5
C(8)-C(9)-H(9)	125.6	C(13)-C(16)-H(16A)	109.5
C(10)-C(9)-H(9)	125.6	C(13)-C(16)-H(16B)	109.5
Ta-C(9)-H(9)	122.3	H(16A)-C(16)-H(16B)	109.5
C(6)-C(10)-C(9)	108.2(7)	C(13)-C(16)-H(16C)	109.5
C(6)-C(10)-Ta	71.4(3)	H(16A)-C(16)-H(16C)	109.5
C(9)-C(10)-Ta	76.0(3)	H(16B)-C(16)-H(16C)	109.5
C(6)-C(10)-H(10)	125.9	C(18)-C(17)-Ta	73.1(5)
C(9)-C(10)-H(10)	125.9	C(18)-C(17)-H(17A)	116.2
Ta-C(10)-H(10)	118.5	Ta-C(17)-H(17A)	116.2
Si-C(11)-H(11A)	109.5	C(18)-C(17)-H(17B)	116.2
Si-C(11)-H(11B)	109.5	Ta-C(17)-H(17B)	116.2
H(11A)-C(11)-H(11B)	109.5	H(17A)-C(17)-H(17B)	113.2
Si-C(11)-H(11C)	109.5	C(17)-C(18)-C(19)	126.9(7)
H(11A)-C(11)-H(11C)	109.5	C(17)-C(18)-Ta	70.1(4)
H(11B)-C(11)-H(11C)	109.5	C(19)-C(18)-Ta	120.8(5)
Si-C(12)-H(12A)	109.5	C(17)-C(18)-H(18)	116.5
Si-C(12)-H(12B)	109.5	C(19)-C(18)-H(18)	116.5
H(12A)-C(12)-H(12B)	109.5	Ta-C(18)-H(18)	79.0
Si-C(12)-H(12C)	109.5	C(20)-C(19)-C(24)	117.2(6)
H(12A)-C(12)-H(12C)	109.5	C(20)-C(19)-C(18)	123.2(7)
H(12B)-C(12)-H(12C)	109.5	C(24)-C(19)-C(18)	119.4(7)
C(8)-C(13)-C(16)	105.7(5)	C(19)-C(20)-C(21)	121.8(7)
C(8)-C(13)-C(14)	113.7(6)	C(19)-C(20)-H(20)	119.1
C(16)-C(13)-C(14)	110.2(7)	C(21)-C(20)-H(20)	119.1
C(8)-C(13)-C(15)	109.7(7)	C(22)-C(21)-C(20)	119.0(8)
C(16)-C(13)-C(15)	107.7(6)	C(22)-C(21)-H(21)	120.5
C(14)-C(13)-C(15)	109.6(5)	C(20)-C(21)-H(21)	120.5
C(13)-C(14)-H(14A)	109.5	C(23)-C(22)-C(21)	119.7(6)
C(13)-C(14)-H(14B)	109.5	C(23)-C(22)-H(22)	120.1
H(14A)-C(14)-H(14B)	109.5	C(21)-C(22)-H(22)	120.1
C(13)-C(14)-H(14C)	109.5	C(22)-C(23)-C(24)	120.9(8)
H(14A)-C(14)-H(14C)	109.5	C(22)-C(23)-H(23)	119.5
H(14B)-C(14)-H(14C)	109.5	C(24)-C(23)-H(23)	119.5
C(13)-C(15)-H(15A)	109.5	C(19)-C(24)-C(23)	121.2(8)
C(13)-C(15)-H(15B)	109.5	C(19)-C(24)-H(24)	119.4
H(15A)-C(15)-H(15B)	109.5	C(23)-C(24)-H(24)	119.4

Table S26. Anisotropic displacement parameters ($Å^2 \times 10^4$) for tBuSpTa(CH_2CHPh)H (22, CCDC 142045). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ta	151(2)	86(1)	171(2)	-53(1)	1(1)	-14(1)
Si	194(10)	120(6)	243(12)	-91(6)	3(8)	-29(6)
C(1)	260(40)	110(20)	180(40)	-90(20)	0(30)	-50(20)
C(2)	230(40)	180(20)	230(40)	-20(20)	-20(30)	-60(20)
C(3)	210(40)	190(20)	210(40)	-50(30)	-120(30)	0(20)
C(4)	100(30)	270(30)	260(40)	-160(30)	50(30)	-80(20)
C(5)	220(40)	220(30)	270(50)	-110(30)	-30(30)	-60(20)
C(6)	150(30)	100(20)	280(40)	-50(20)	-50(30)	20(20)
C(7)	180(30)	75(19)	260(40)	-60(20)	-40(30)	-10(20)
C(8)	190(40)	110(20)	230(40)	-80(20)	-20(30)	0(20)
C(9)	150(30)	140(20)	190(40)	-70(20)	-90(30)	10(20)
C(10)	190(30)	100(20)	260(40)	-40(20)	-10(30)	-30(20)
C(11)	340(40)	230(20)	300(50)	-200(30)	20(40)	-40(30)
C(12)	320(40)	160(20)	370(50)	-90(30)	-20(40)	-90(30)
C(13)	140(30)	170(20)	250(40)	-40(20)	0(30)	-60(20)
C(14)	320(40)	270(30)	250(50)	-50(30)	60(30)	-210(30)
C(15)	310(40)	170(20)	370(50)	-120(30)	30(40)	-110(20)
C(16)	230(40)	190(20)	520(60)	-50(30)	-110(40)	-100(20)
C(17)	220(40)	170(20)	250(40)	-30(20)	-60(30)	-30(20)
C(18)	140(30)	190(20)	200(40)	-120(20)	60(30)	-50(20)
C(19)	290(40)	210(20)	180(40)	-90(30)	-30(30)	-70(30)
C(20)	250(40)	200(20)	300(50)	-130(30)	30(30)	-50(20)
C(21)	160(40)	340(30)	390(50)	-200(30)	30(30)	-20(30)
C(22)	310(50)	220(30)	340(50)	-90(30)	-40(40)	-20(30)
C(23)	280(40)	190(20)	310(50)	-70(30)	-10(40)	-40(30)
C(24)	210(40)	210(30)	260(50)	-110(30)	30(30)	-30(20)

Table S27. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for tBuSpTa(CH_2CHPh)H (22, CCDC 142045).

	x	y	z	U_{iso}
H	5763	9137	6688	50
H(2)	6070(80)	7674(15)	4750(70)	27
H(3)	3925(19)	9820(70)	5170(30)	26
H(4)	2665	8516	6894	23
H(5)	3810(30)	5850(70)	7340(60)	28
H(7)	8560(30)	6600(30)	6030(90)	21
H(9)	7563(16)	6440(20)	9620(80)	20
H(10)	6970(40)	4540(60)	9250(50)	23
H(11A)	9050(50)	3480(60)	5327(17)	43
H(11B)	8300(50)	5030(50)	4610(40)	43
H(11C)	7770(30)	3900(60)	4500(40)	43
H(12A)	7350(50)	2150(50)	7480(50)	42
H(12B)	5990(60)	2780(40)	6640(30)	42
H(12C)	5910(60)	3180(30)	7900(50)	42
H(14A)	9610(60)	8120(30)	5990(30)	38
H(14B)	9670(50)	9440(50)	6573(10)	38
H(14C)	8070(50)	9480(50)	6190(30)	38
H(15A)	8070(60)	8420(30)	9540(50)	40
H(15B)	7260(60)	9630(60)	8340(40)	40
H(15C)	8760(40)	9520(60)	8760(50)	40
H(16A)	10810(40)	6500(60)	8070(50)	46
H(16B)	10380(9)	6650(60)	9060(50)	46
H(16C)	10840(40)	7450(30)	8400(60)	46
H(17A)	3510(60)	7238(6)	9086(9)	27
H(17B)	4940(30)	6530(40)	9930(50)	27
H(18)	5320(100)	8566(6)	8897(9)	20
H(20)	1772	9432	8664	30
H(21)	70(120)	11702(16)	8072(9)	36
H(22)	580(60)	13780(80)	7530(20)	37
H(23)	2950(30)	13240(80)	7630(20)	33
H(24)	4640(110)	11125(13)	8177(8)	28

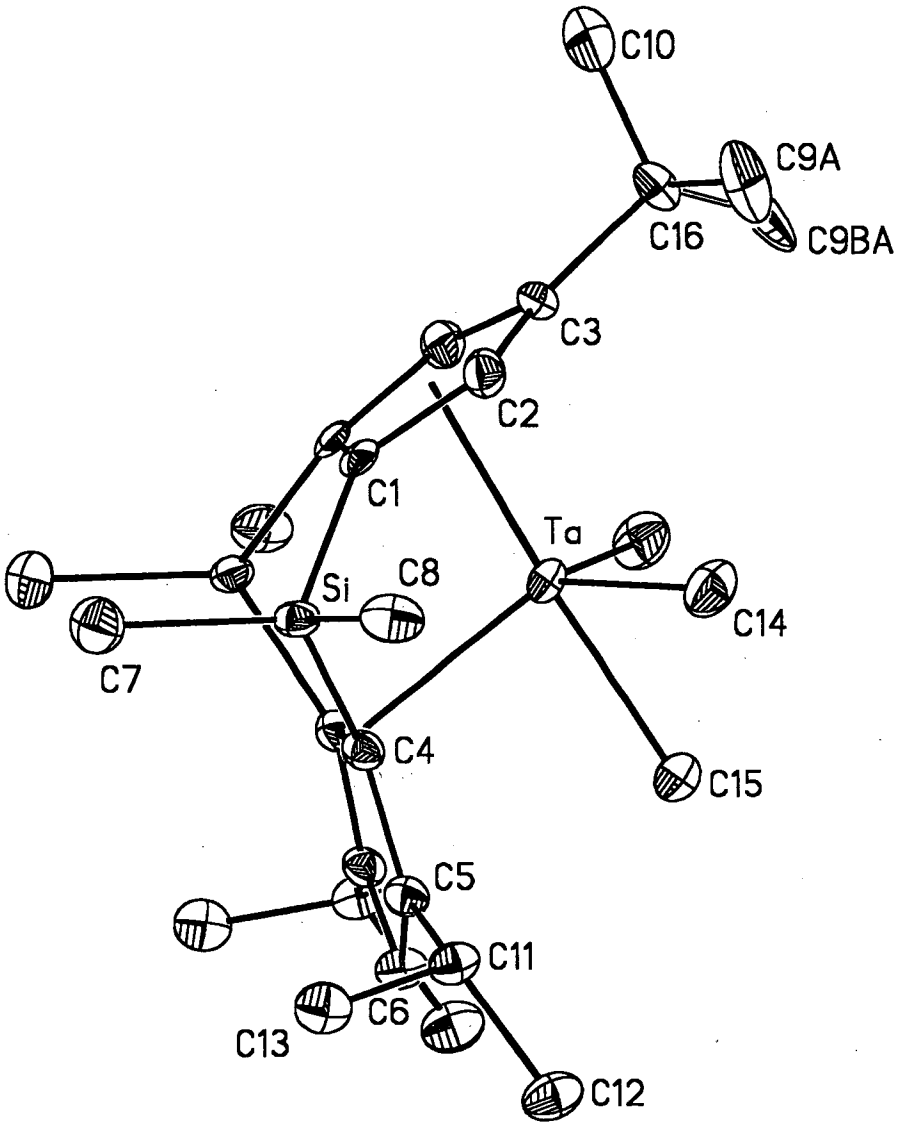

Figure S1. Molecular structure of **23** with 50% probability ellipsoids. Hydrogen atoms have been omitted. The molecule is bisected by a crystallographic mirror plane containing atoms Ta, C3, C6, C15, and C16. Only one of the two equally-populated disordered t-butyl groups is shown. This compound is isostructural with the TMS analog.

Table S28. Crystal Data and Structure Analysis Details for $[(Me_2Si)_2(\eta^5\text{-}4\text{-}CMe_3\text{-}C_5H_2)(\eta^2\text{-}3,5\text{-}CMe_2H\text{-}C_5H_1)]TaMe_3$ (23, CCDC 147415).

Empirical formula	$C_{27}H_{46}Si_2Ta$
Formula weight	607.77
Crystallization solvent	diethyl ether / petroleum ether
Crystal shape	tapered block
Crystal color	tangerine
Crystal size	0.19 x 0.28 x 0.33 mm

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker SMART 1000 ccd	
Wavelength	0.71073 Å MoKα	
Data collection temperature	98 K	
Theta range for 7898 reflections used in lattice determination	2.4 to 28.5°	
Unit cell dimensions	a = 16.9762(8) Å b = 16.2378(8) Å c = 9.8844(5) Å	α= 90° β= 90° γ = 90°
Volume	2724.7(2) $Å^3$	
Z	4	
Crystal system	orthorhombic	
Space group	*Pnma* (# 62)	
Density (calculated)	1.482 g/cm^3	
F(000)	1236	
Theta range for data collection	2.38 to 28.54°	
Completeness to theta = 28.54°	96.6 %	
Index ranges	$-22 \le h \le 22, -21 \le k \le 21, -13 \le l \le 12$	
Data collection scan type	ω scans at 6 fixed φ values	
Reflections collected	46479	
Independent reflections	3468 [R_{int}= 0.0698]	
Reflections > 2σ(I)	3219	
Average σ(I)/(net I)	0.0216	
Absorption coefficient	4.134 mm^{-1}	
Absorption correction	none	
Number of standards	first scans recollected at end of runs	
Decay of standards	within counting statistics	

Table S28 (cont.)

Structure Solution and Refinement

Primary solution method	direct methods
Secondary solution method	difference map
Hydrogen placement	calculated
Refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	3468 / 0 / 157
Treatment of hydrogen atoms	not refined, U_{iso} fixed at 120% U_{eq} of attached atom
Goodness-of-fit on F^2	2.547
Final R indices [I>2σ(I), 3219 reflections]	R1 = 0.0450, wR2 = 0.1515
R indices (all data)	R1 = 0.0479, wR2 = 0.1545
Type of weighting scheme used	sigma
Weighting scheme used	$w=1/[\sigma^2(F_o^2) + (0.05P)^2]$
Max shift/error	0.020
Average shift/error	0.001
Largest diff. peak and hole	10.876 and -4.558 $e \cdot Å^{-3}$

Programs Used

Cell refinement	Bruker SAINT v6.02
Data collection	Bruker SMART v5.606
Data reduction	Bruker SAINT v6.02
Structure solution	Bruker SHELXTL v5.1
Structure refinement	Bruker SHELXTL v5.1

Special Refinement Details

A tapered block was cut from a large irregular lumpish tangerine-colored crystal and was mounted on a glass fiber with Paratone-N oil. Six runs of data were collected with 18 second long, –0.25° wide ω–scans at six values of φ (0, 120, 240, 60, 180, 90 and 300°) with the detector 5 cm (nominal) distant at a θ of -28°. The initial cell for data reduction was calculated from just under 1000 reflections chosen from throughout the data frames. For data processing with SAINT v6.02, all defaults were used, except: a fixed box size of 1.8 x 1.8 x 0.6 was used, profiles for the nine detector areas were blended, periodic orientation matrix updating was disabled, the instrument error was set to zero, no Laue class integration restraints were used, and for the post-integration global least squares refinement, no constraints were applied. No decay correction was needed. A data set corrected with SADABS v. 2.0 (beta) showed no improvement and consequently was not used. The data were intense and a weighting scheme of $w=1/[\sigma^2(F_o^2) + (0.05P)^2]$ was used, where $P = [2F_c^2 + \max(F_o^2,0)] / 3$.

There is _ molecule in the asymmetric unit; the molecule lies on the mirror plane (Wyckoff site *c*). The mirror plane bisects both cyclopentadienyl rings and contains five atoms: Ta, C3 and C6 (cyclopentadienyl carbons), C15 (central tantalum methyl carbon), and C16 (*t*-butyl carbon).

The three methyl carbons on the *t*-butyl group are disordered about the mirror plane; consequently the population ratio is 50:50. This disorder is common in similar *t*-butyl substituted metallocenes. In particular this compound is essentially isostructural with the trimethysilyl-substituted analog, $TMSThpTaMe_3$ (PJC 22). These structures differ in the orientation of the 4-substituent on the cyclopentadienyl ring; in the latter case, one of the silyl-methyl bonds is oriented towards the center of the metallocene wedge. The orientation of this substituent is rotated 180° with respect to the *t*-butyl substituent of this structure.

No reflections were specifically omitted from the final processed dataset; 2369 reflections were rejected, with 50 space group-absence violations, 218 inconsistent equivalents and no reflections suppressed. Refinement of F^2 was against all reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement.

This dataset is typical for a tantalum containing compound on the CCD. There are many large peaks in the final difference map; the eight greater than |1| $e\cdot Å^{-3}$ are: 10.88, -4.56, -1.67, 1.61, -1.60 and 1.19 $e\cdot Å^{-3}$ at 0.55 to 1.37Å from Ta, 1.01 $e\cdot Å^{-3}$ at 0.47Å from C10 and 1.01 $e\cdot Å^{-3}$ at 0.84Å from C4.

Table S29. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [$(Me_2Si)_2(\eta^5$-4-CMe_3-$C_5H_2)(\eta^2$-3,5-CMe_2H-C_5H_1)]$TaMe_3$ (23, CCDC 147415). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ta	646(1)	2500	4816(1)	16(1)
Si	650(1)	3576(1)	2134(2)	16(1)
C1	1435(2)	2949(3)	2951(4)	14(1)
C2	1882(2)	3194(3)	4099(5)	19(1)
C3	2174(4)	2500	4821(6)	19(1)
C4	-165(2)	2961(3)	2891(5)	15(1)
C5	-952(2)	3204(3)	3187(5)	16(1)
C6	-1431(3)	2500	3310(7)	19(1)
C7	679(3)	3608(6)	243(6)	29(2)
C8	755(3)	4663(3)	2734(7)	25(1)
C9A [a]	2867(9)	3456(8)	6559(13)	41(3)
C10 [a]	3545(7)	2257(10)	5460(12)	49(5)
C9B [a]	2518(8)	3019(10)	7107(13)	54(4)
C11	-1225(2)	4088(3)	3367(5)	18(1)
C12	-1969(3)	4158(3)	4239(6)	25(1)
C13	-1377(3)	4498(3)	1997(5)	24(1)
C14	692(3)	3640(4)	6044(7)	28(1)
C15	-470(4)	2500	5990(8)	25(2)
C16	2755(4)	2500	5989(7)	24(1)

[a] Population: _

Table S30. Bond lengths [Å] and angles [°] for [$(Me_2Si)_2(\eta^5$-4-CMe_3-$C_5H_2)(\eta^2$-3,5-CMe_2H-$C_5H_1)$]$TaMe_3$ (23, CCDC 147415).

Ta-C1	2.392(4)	C13-H13B	0.9600
Ta-C2	2.484(4)	C13-H13C	0.9600
Ta-C3	2.593(7)	C14-H14A	0.9600
Ta-C4	2.465(4)	C14-H14B	0.9600
Ta-C14	2.215(6)	C14-H14C	0.9600
Ta-C15	2.222(7)	C15-H15A	0.9684
Ta···PlnA [a]	2.140(3)	C15-H15B	0.9563
Ta···PlnB [b]	2.129(7)		
Ta-CpA [c]	2.150	C14-Ta-C14^i	113.4(4)
Ta···CpB [d]	2.895	C14-Ta-C15	75.15(16)
Ta-Cen [e]	2.349	PlnA-PlnB	112.75(24)
Si-C1	1.862(4)	CpA-Ta···CpB	115.7
Si-C4	1.863(4)	CpA-Ta-Cen	97.6
Si-C7	1.870(6)	CpA-Ta-C14	103.3
Si-C8	1.871(6)	CpA-Ta-C15	176.8
C1-C2	1.422(6)	Cen-Ta-C14	117.7
C1-C1^i	1.458(9)	Cen-Ta-C15	85.6
C2-C3	1.423(6)	C1-Si-C4	93.7(2)
C2-H2	0.9300	C1-Si-C7	115.4(3)
C3-C16	1.518(9)	C4-Si-C7	115.9(3)
C4-C5	1.423(6)	C1-Si-C8	108.1(2)
C4-C4^i	1.499(9)	C4-Si-C8	116.6(2)
C5-C6	1.408(5)	C7-Si-C8	106.8(4)
C5-C11	1.518(6)	C2-C1-C1^i	106.3(3)
C6-H6	0.9300	C2-C1-Si	125.1(3)
C7-H7A	0.9600	C1^i-C1-Si	123.17(14)
C7-H7B	0.9600	C1-C2-C3	111.4(4)
C7-H7C	0.9600	C1-C2-H2	124.3
C8-H8A	0.9600	C3-C2-H2	124.3
C8-H8B	0.9600	C2^i-C3-C2	104.7(5)
C8-H8C	0.9600	C2-C3-C16	127.4(3)
C9A-C16	1.663(12)	C5-C4-C4^i	106.1(3)
C9A-H9A	0.9600	C5-C4-Si	129.1(3)
C9A-H9B	0.9600	C4^i-C4-Si	122.40(14)
C9A-H9C	0.9600	C6-C5-C4	109.5(4)
C10-C16	1.493(14)	C6-C5-C11	125.6(4)
C10-H10A	0.9600	C4-C5-C11	124.9(4)
C10-H10B	0.9600	C5-C6-C5^i	108.6(5)
C10-H10C	0.9600	C5-C6-H6	125.7
C9B-C16	1.447(13)	Si-C7-H7A	109.5
C9B-H9D	0.9600	Si-C7-H7B	109.5
C9B-H9E	0.9600	H7A-C7-H7B	109.5
C9B-H9F	0.9600	Si-C7-H7C	109.5
C11-C13	1.532(6)	H7A-C7-H7C	109.5
C11-C12	1.534(6)	H7B-C7-H7C	109.5
C11-H11	0.9800	Si-C8-H8A	109.5
C12-H12A	0.9600	Si-C8-H8B	109.5
C12-H12B	0.9600	H8A-C8-H8B	109.5
C12-H12C	0.9600	Si-C8-H8C	109.5
C13-H13A	0.9600	H8A-C8-H8C	109.5

H8B-C8-H8C	109.5	C11-C12-H12B	109.5
C16-C9A-H9A	109.5	H12A-C12-H12B	109.5
C16-C9A-H9B	109.5	C11-C12-H12C	109.5
H9A-C9A-H9B	109.5	H12A-C12-H12C	109.5
C16-C9A-H9C	109.5	H12B-C12-H12C	109.5
H9A-C9A-H9C	109.5	C11-C13-H13A	109.5
H9B-C9A-H9C	109.5	C11-C13-H13B	109.5
C16-C10-H10A	109.5	H13A-C13-H13B	109.5
C16-C10-H10B	109.5	C11-C13-H13C	109.5
H10A-C10-H10B	109.5	H13A-C13-H13C	109.5
C16-C10-H10C	109.5	H13B-C13-H13C	109.5
H10A-C10-H10C	109.5	Ta-C14-H14A	109.5
H10B-C10-H10C	109.5	Ta-C14-H14B	109.5
C16-C9B-H9D	109.5	H14A-C14-H14B	109.5
C16-C9B-H9E	109.5	Ta-C14-H14C	109.5
H9D-C9B-H9E	109.5	H14A-C14-H14C	109.5
C16-C9B-H9F	109.5	H14B-C14-H14C	109.5
H9D-C9B-H9F	109.5	Ta-C15-H15A	109.2
H9E-C9B-H9F	109.5	Ta-C15-H15B	109.7
C5-C11-C13	111.0(4)	H15A-C15-H15B	109.1
C5-C11-C12	112.8(4)	C9B-C16-C10^{i}	111.3(10)
C13-C11-C12	109.0(4)	C9B-C16-C3	113.6(6)
C5-C11-H11	108.0	C10-C16-C3	108.5(7)
C13-C11-H11	108.0	C9B-C16-C9A^{i}	108.5(11)
C12-C11-H11	108.0	C10-C16-C9A	105.2(9)
C11-C12-H12A	109.5	C3-C16-C9A	109.4(5)

Symmetry transformations used to generate equivalent atoms: (i) x,-y+1/2,z

[a] PlnA is the best plane through atoms C1, C2, C3, C1^{i} and C2^{i}

[b] PlnB is the best plane through atoms C4, C5, C6, C4^{i} and C5^{i}

[c] CpA is the centroid of atoms C1, C2, C3, C1^{i} and C2^{i}

[d] CpB is the centroid of atoms C4, C5, C6, C4^{i} and C5^{i}

[e] Cen is the centroid of atoms C4 and C4^{i}

Table S31. Anisotropic displacement parameters ($Å^2 \times 10^4$) for [$(Me_2Si)_2(\eta^5$-4-CMe_3-$C_5H_2)(\eta^2$-3,5-CMe_2H-$C_5H_1)$]$TaMe_3$ (23, CCDC 147415). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ta	161(2)	169(2)	137(2)	0	46(1)	0
Si	116(6)	175(7)	180(7)	35(6)	9(4)	-15(4)
C1	113(18)	180(20)	130(20)	33(17)	64(15)	-18(15)
C2	200(20)	200(20)	160(20)	-23(17)	0(17)	-17(16)
C3	120(30)	290(40)	150(30)	0	-20(20)	0
C4	144(19)	160(20)	150(20)	33(17)	-17(17)	-5(16)
C5	144(19)	170(20)	170(20)	9(17)	-21(17)	28(16)
C6	150(30)	170(30)	250(30)	0	20(20)	0
C7	290(40)	340(40)	230(40)	80(20)	11(17)	-30(20)
C8	210(20)	190(20)	350(30)	40(20)	-20(20)	-30(17)
C9A	610(80)	370(70)	240(60)	-60(50)	-150(60)	-20(60)
C10	400(60)	820(160)	250(50)	-110(60)	-80(50)	140(60)
C9B	510(80)	820(100)	280(70)	-320(70)	-270(60)	350(70)
C11	159(19)	140(20)	250(20)	-22(18)	22(17)	1(15)
C12	220(20)	200(20)	340(30)	-30(20)	50(20)	33(17)
C13	240(20)	190(20)	290(30)	0(20)	-11(19)	12(17)
C14	280(30)	280(30)	270(30)	-60(30)	71(18)	24(18)
C15	210(30)	360(40)	190(30)	0	40(30)	0
C16	200(30)	340(40)	180(30)	0	-70(30)	0

Table S32. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$ x 10^3) for [$(Me_2Si)_2(\eta^5$-4-CMe_3-$C_5H_2)(\eta^2$-3,5-CMe_2H-$C_5H_1)$]$TaMe_3$ (23, CCDC 147415).

	x	y	z	U_{iso}
H(2)	197	374	435	23
H(6)	-197	250	345	23
H(7A)	63	306	-11	34
H(7B)	117	384	-5	34
H(7C)	25	394	-9	34
H(8A)	74	468	370	30
H(8B)	33	499	238	30
H(8C)	125	488	242	30
H(9A)	323	346	730	49
H(9B)	237	366	686	49
H(9C)	306	380	585	49
H(10A)	349	208	454	59
H(10B)	375	182	600	59
H(10C)	389	272	550	59
H(9D)	219	271	771	64
H(9E)	223	349	677	64
H(9F)	298	321	758	64
H(11)	-80	439	382	22
H(12A)	-188	391	510	31
H(12B)	-240	388	380	31
H(12C)	-210	473	436	31
H(13A)	-91	446	144	29
H(13B)	-150	507	213	29
H(13C)	-181	423	155	29
H(14A)	17	382	624	33
H(14B)	97	406	555	33
H(14C)	97	353	688	33
H(15A)	-91	250	537	30
H(15B)	-50	298	654	30

[a] Population: _

Least-squares planes (x,y,z in crystal coordinates) and deviations from them
(* indicates atom used to define plane)

14.0644 (0.0294) x - 0.0000 (0.0002) y - 5.5355 (0.0253) z = 0.3826 (0.0146)

* 0.0019 (0.0013) C1
* -0.0049 (0.0033) C2
* 0.0060 (0.0040) C3
* 0.0019 (0.0013) C1_$1
* -0.0049 (0.0033) C2_$1
-2.1395 (0.0027) Ta

Rms deviation of fitted atoms = 0.0043

3.3294 (0.0578) x - 0.0000 (0.0001) y + 9.6924 (0.0068) z = 2.7541 (0.0070)

Angle to previous plane (with approximate esd) = 67.25 (0.24)

* -0.0067 (0.0012) C4
* 0.0179 (0.0033) C5
* -0.0224 (0.0041) C6
* -0.0067 (0.0012) C4_$1
* 0.0179 (0.0033) C5_$1
2.1291 (0.0074) Ta

Rms deviation of fitted atoms = 0.0157

Principal mean square atomic displacements U

0.0196	0.0169	0.0101	Ta
0.0213	0.0150	0.0107	Si
0.0201	0.0176	0.0046	C1
0.0224	0.0189	0.0152	C2
0.0291	0.0158	0.0109	C3
0.0193	0.0143	0.0117	C4
0.0191	0.0181	0.0118	C5
0.0248	0.0171	0.0144	C6
0.0388	0.0290	0.0181	C7
0.0367	0.0220	0.0166	C8
0.0660	0.0389	0.0167	C9A_a
0.0889	0.0373	0.0211	C10_a
0.1234	0.0289	0.0085	C9B_b
0.0255	0.0155	0.0135	C11
0.0363	0.0240	0.0159	C12
0.0294	0.0239	0.0190	C13
0.0357	0.0307	0.0169	C14
0.0361	0.0240	0.0154	C15
0.0343	0.0265	0.0118	C16

Electron density synthesis with coefficients Fo-Fc

Highest peak 10.88 at 0.0282 0.2500 0.4361 [0.76 A from TA]
Deepest hole -4.56 at 0.0932 0.2500 0.5162 [0.59 A from TA]

Mean = 0.00, Rms deviation from mean = 0.22 e/A^3, Highest memory used = 3300 / 28101

Fourier peaks appended to .res file

	x	y	z	sof	U	Peak	Distances to nearest atoms (including symmetry equivalents)
Q1	1	0.0282	0.2500	0.4361	0.50000	0.05	10.88 0.76 TA 1.80 C4 2.06 C15 2.26 H15A
Q2	1	0.0932	0.2500	0.5162	0.50000	0.05	-4.56 0.59 TA 2.09 C14 2.14 C3 2.23 C2
Q3	1	-0.0121	0.2500	0.4401	0.50000	0.05	-1.67 1.37 TA 1.65 H15A 1.67 C4 1.68 C15
Q4	1	0.3560	0.2500	0.5198	0.50000	0.05	1.66 0.47 C10 0.73 H10C 0.96 H10A 1.40 H10B
Q5	1	0.0611	0.2265	0.5212	1.00000	0.05	1.61 0.55 TA 1.69 C14 2.03 C15 2.17 H14A
Q6	1	0.0376	0.2500	0.5033	0.50000	0.05	-1.60 0.51 TA 1.72 C15 2.17 C14 2.21 H15A
Q7	1	0.1090	0.2500	0.5597	0.50000	0.05	1.19 1.08 TA 1.99 C3 2.02 C14 2.11 H14C
Q8	1	0.0023	0.2612	0.3430	1.00000	0.05	1.01 0.84 C4 1.12 C4 1.74 TA 1.93 C5
Q9	1	-0.0298	0.2500	0.6829	0.50000	0.05	0.84 0.88 C15 0.90 H15B 1.78 H15A 2.36 H14A
Q10	1	0.0257	0.2500	0.3575	0.50000	0.05	-0.83 1.24 C4 1.39 TA 2.22 C1 2.35 SI
Q11	1	0.1795	0.2500	0.5017	0.50000	0.05	0.81 0.67 C3 1.45 C2 1.89 C16 1.96 TA
Q12	1	0.1508	0.2500	0.5000	0.50000	0.05	-0.77 1.14 C3 1.47 TA 1.57 C2 2.16 C1
Q13	1	-0.0562	0.2500	0.4446	0.50000	0.05	-0.70 1.09 H15A 1.53 C15 1.82 C5 1.84 C4
Q14	1	0.0631	0.3566	0.1325	1.00000	0.05	0.69 0.80 SI 1.07 C7 1.64 H7A 1.65 H7C
Q15	1	0.0233	0.2500	0.6204	0.50000	0.05	0.62 1.21 C15 1.50 H15B 1.54 TA 2.01 C14
Q16	1	0.2847	0.2500	0.4403	0.50000	0.05	-0.61 1.21 C3 1.31 H10A 1.58 C16 1.63 C10
Q17	1	0.3764	0.2901	0.5453	1.00000	0.05	-0.60 0.37 H10C 0.45 C10 0.71 H10B 1.01 H10A
Q18	1	0.2357	0.2500	0.6436	0.50000	0.05	0.58 0.81 C16 1.11 C9B 1.34 H9D 1.63 C3
Q19	1	-0.1176	0.2500	0.3974	0.50000	0.05	0.57 0.79 C6 1.43 C5 1.45 H6 1.45 H15A
Q20	1	-0.0698	0.3023	0.5880	1.00000	0.05	0.56 0.74 H15B 0.94 C15 1.05 H15A 1.79 H15B

Shortest distances between peaks (including symmetry equivalents)

8 8 0.36	8 10 0.46	11 12 0.49	2 7 0.51	5 6 0.58	2 5 0.67	1 6 0.68
1 3 0.69	3 13 0.75	5 5 0.76	1 10 0.78	4 17 0.78	7 12 0.92	2 6 0.95
5 7 0.97	2 12 0.99	3 8 1.01	1 8 1.04	3 10 1.04	3 6 1.05	1 5 1.08
9 15 1.09	13 19 1.14	6 15 1.18	5 15 1.23	17 17 1.30	7 11 1.33	6 7 1.33
1 2 1.36	8 13 1.42	1 13 1.43	9 20 1.44	4 16 1.44	6 10 1.46	2 11 1.47
3 5 1.53	2 15 1.57	7 15 1.57	5 12 1.58	10 13 1.63	13 20 1.67	6 13 1.69
11 18 1.70	20 20 1.70	6 8 1.70	5 10 1.77	15 20 1.82	1 15 1.82	1 7 1.84
3 19 1.84	3 15 1.88	11 16 1.89	6 12 1.92	2 3 1.94	2 10 1.94	3 20 1.95
16 17 1.98	12 18 2.02	5 8 2.03	5 11 2.05	5 8 2.10	6 9 2.11	8 19 2.11
5 13 2.16	1 12 2.17	16 18 2.17	6 20 2.18	13 15 2.20	19 20 2.22	5 9 2.25
7 18 2.30	2 8 2.31	12 16 2.35	5 20 2.37	3 7 2.37	4 18 2.38	1 20 2.40
9 13 2.40	6 11 2.41	3 9 2.42	7 10 2.45	10 19 2.47	12 15 2.47	1 19 2.51
10 12 2.55	10 15 2.60	5 20 2.63	1 9 2.63	2 13 2.63	1 11 2.65	7 9 2.65
2 9 2.66	17 18 2.66	2 18 2.73	8 15 2.77	8 14 2.79	8 20 2.79	7 8 2.81
3 12 2.83	6 19 2.84	10 14 2.89	11 15 2.90	8 20 2.90	10 20 2.92	8 12 2.97
10 11 2.97	2 20 2.98					

Table S33. Crystal Data and Structure Analysis Details for [$(Me_2Si)_2(\eta^5$-4-CMe_3-$C_5H_2)(\eta^5$-3,5-CMe_2H-$C_5H_1)$]Ta$(CH_2)CH_3$ (24, CCDC 147413).

Empirical formula	$C_{26}H_{43}Si_2Ta$
Formula weight	592.73
Crystallization solvent	diethyl ether / pentane
Crystal shape	twinned plate
Crystal color	golden orange
Crystal size	0.07 x 0.18 x 0.19 mm

Data Collection

Type of diffractometer	CAD-4	
Wavelength	0.71073 Å MoKα	
Data collection temperature	84 K	
Theta range for 25 reflections used in lattice determination	13 to 18°	
Unit cell dimensions	a = 8.508(3) Å b = 16.123(6) Å c = 9.984(3) Å	α= 90° β= 112.39(3)° γ = 90°
Volume	1266.3(8) $Å^3$	
Z	2	
Crystal system	monoclinic	
Space group	$P2_1/m$ (# 11)	
Density (calculated)	1.555 g/cm^3	
F(000)	600	
Theta range for data collection	2.21 to 25°	
Completeness to theta = 25°	71.5 %	
Index ranges	$-10 \le h \le 10, -19 \le k \le 19, -11 \le l \le 11$	
Data collection scan type	ω-scan	
Reflections collected	11978	
Independent reflections	1651 [R_{int}= 0.050; GOF_{merge}= 1.58]	
Reflections > 2σ(I)	1576	
Average σ(I)/(net I)	0.0256	
Absorption coefficient	4.445 mm^{-1}	
Absorption correction	ψ-scan	
Max. and min. transmission	1.16 and 0.84	
Number of standards	3 reflections measured every 75 min	
Decay of standards	0.5%	

Table S33 (cont.)

Structure Solution and Refinement

Primary solution method	direct methods
Secondary solution method	difference map
Hydrogen placement	calculated
Refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	1651 / 0 / 140
Treatment of hydrogen atoms	not refined, U_{iso} fixed at 120% U_{eq} of attached atom
Goodness-of-fit on F^2	2.385
Final R indices [I>2σ(I), 1576 reflections]	R1 = 0.0274, wR2 = 0.0659
R indices (all data)	R1 = 0.0297, wR2 = 0.0664
Type of weighting scheme used	sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.017
Average shift/error	0.001
Largest diff. peak and hole	1.577 and -0.823 $e \cdot Å^{-3}$

Programs Used

Cell refinement	CAD-4 Software (Enraf-Nonius, 1989)
Data collection	CAD-4 Software (Enraf-Nonius, 1989)
Data reduction	CRYM (Duchamp, 1964)
Structure solution	Bruker SHELXTL v5.1
Structure refinement	Bruker SHELXTL v5.1

Special Refinement Details

The crystals grow as twinned, golden orange plates. Samples were mounted on a glass fibers with Paratone-N oil. Finally a crystal was found for which a unit cell could be determined. Although this crystal was also twinned, orientation matrixes were obtained for both twin components. The reflection indices (h k l) and (h' k' l') for the two twin components are related as:

$$\begin{pmatrix} h' & k' & l' \end{pmatrix} = \begin{matrix} -1 & 0 & 0.65 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix} \leftarrow \begin{matrix} h \\ k \\ l \end{matrix}$$

The twin may be described as a reflection twin across the [1 0 0] plane ; the corresponding reciprocal space description is a rotation twin about the $(1\ 0\ 0)^*$ axis as this axis is normal to the [1 0 0] plane. Since by the monoclinic symmetry, (h k l) is equivalent to (h k̄ l), two interpretations of the reciprocal lattice overlap are shown as additional figures. Data were collected with 1.0° ω-scans. Data which agreed poorly in a preliminary merging were recollected. The individual backgrounds were replaced by a background function of 2θ derived from those reflections with $I < 3\sigma(I)$. The first attempts at refinement included all measured reflections; those reflections which presumably included overlap between the two twin components were given two sets of indices corresponding to the two twins. A twin parameter relating the relative contributions of the two components was included in the least squares matrix. Various criteria were used to identified overlapping reflections. However none of these approaches were particularly successful, presumably since most reflections do not perfectly coincide. The measured intensities of these reflections would then not reflect the true sum of the two contributing components. Finally, all reflections with $l = 3$, 6, 9 and 11 were removed from the dataset; these reflections transform with h' deviating from integral values by 0.05, 0.10, 0.15 and 0.15, respectively. Therefore only the (h k 0) reflections, which overlap perfectly with the (h $-k$ 0) reflections of the twin, contain any twin contribution. The (h $-k$ 0) reflections were added as the symmetry equivalent (h k 0) form. The GOF_{merge} was 1.58 (1651 multiples) in point group 2/m; due to the high redundancy of the data, there were no duplicates from which to calculate R_{merge}. Ψ–scan data were used for the absorption correction. There was 0.5% linear decay. No outlier reflections were omitted from the refinement.

Weights w are calculated as $1/\sigma^2(F_o^2)$; variances ($\sigma^2(F_o^2)$) were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\langle I\rangle)^2$. The refinement of F^2 is as always against all reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement.

The molecule lies on a mirror plane containing the Ta and bisecting both Cp rings; there is _ molecule in the asymmetric unit. The *t*-butyl group is disordered about the mirror plane, as is seen in similar compounds. Splitting the three methyl carbon atoms into two sites each did not improve the model, so these atoms were left at single sites with elongated displacement ellipsoids. Unfortunately, the mirror plane also confuses the $=CH_2$ and $-CH_3$ groups bound to the Ta. The principal axis of the displacement ellipsoid is perpendicular to the Ta to C bond. The hydrogen atoms on this C15 were modeled with three calculated sites, as a normal CH_3 group with one hydrogen atom pointing up with population one and the other two hydrogen atoms with population _. All hydrogen atoms were placed at calculated positions with U_{iso}'s fixed at 120% of the U_{eq} of the attached atom.

The minor twin component refined to a fractional population of 0.168(4). There are only two peaks greater than |1| e·Å^{-3} in the final difference map: 1.57 e·Å^{-3} (1.75Å from H6) and 1.07 e·Å^{-3} (0.79Å from H6).

Table S34. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [$(Me_2Si)_2(\eta^5$-4-CMe_3-$C_5H_2)(\eta^5$-3,5-CMe_2H-C_5H_1)]Ta(CH_2)CH_3 (24, CCDC 147413). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ta	9041(1)	2500	404(1)	8(1)
Si	8700(2)	1425(1)	2918(2)	13(1)
C1	7103(6)	2051(3)	1440(6)	12(1)
C2	6321(6)	1796(3)	-25(6)	11(1)
C3	5783(9)	2500	-945(10)	12(2)
C4	10527(6)	2051(3)	2808(6)	9(1)
C5	11652(6)	1783(3)	2128(6)	10(1)
C6	12270(9)	2500	1669(9)	10(2)
C7	8466(8)	1417(4)	4693(7)	26(2)
C8	8542(7)	332(3)	2300(7)	21(1)
C9	4584(10)	2500	-2519(10)	17(2)
C10	3500(17)	1781(9)	-2847(12)	203(11)
C11	5439(17)	2500	-3560(15)	124(9)
C12	12261(7)	901(3)	2070(7)	14(1)
C13	13116(7)	555(3)	3585(7)	19(1)
C14	13493(7)	851(3)	1294(7)	18(1)
C15	9207(8)	1482(4)	-933(7)	27(2)

Table S35. Bond lengths [Å] and angles [°] for $[(Me_2Si)_2(\eta^5\text{-}4\text{-}CMe_3\text{-}C_5H_2)(\eta^5\text{-}3,5\text{-}CMe_2H\text{-}C_5H_1)]Ta(CH_2)CH_3$ (24, CCDC 147413).

Ta-CpA [a]	2.129	C15-H15C	0.9800
Ta-CpB [c]	2.139		
Ta···PlnA [b]	2.117(4)	CpA-Ta-CpB	125.4
Ta···PlnB [d]	2.126(4)	CpA-Ta-C15	107.1
Ta-C15	2.155(7)	CpB-Ta-C15	107.4
Ta-C4	2.360(6)	PlnA-PlnB	67.0(3)
Ta-C1	2.369(5)	C15-Ta-C15$^{(i)}$	99.3(4)
Ta-C2	2.464(5)	C8-Si-C7	106.9(3)
Ta-C5	2.514(5)	C8-Si-C1	108.1(3)
Ta-C6	2.549(7)	C7-Si-C1	116.5(3)
Ta-C3	2.579(7)	C8-Si-C4	116.4(3)
Si-C8	1.856(6)	C7-Si-C4	116.7(3)
Si-C7	1.857(7)	C1-Si-C4	91.9(2)
Si-C1	1.874(6)	C2-C1-C1$^{(i)}$	106.8(3)
Si-C4	1.891(5)	C2-C1-Si	124.8(4)
C1-C2	1.418(8)	C1$^{(i)}$-C1-Si	122.55(17)
C1-C1$^{(i)}$	1.449(10)	C1-C2-C3	110.1(5)
C2-C3	1.422(7)	C1-C2-H2	124.9
C2-H2	0.9500	C3-C2-H2	124.9
C3-C9	1.513(12)	C2$^{(i)}$-C3-C2	106.0(7)
C4-C5	1.434(8)	C2-C3-C9	126.5(4)
C4-C4$^{(i)}$	1.448(10)	C5-C4-C4$^{(i)}$	107.5(3)
C5-C6	1.416(7)	C5-C4-Si	125.4(4)
C5-C12	1.523(7)	C4$^{(i)}$-C4-Si	122.23(16)
C6-H6	0.9500	C6-C5-C4	107.7(5)
C7-H7A	0.9800	C6-C5-C12	125.2(5)
C7-H7B	0.9800	C4-C5-C12	126.7(5)
C7-H7C	0.9800	C5-C6-C5$^{(i)}$	109.4(7)
C8-H8A	0.9800	C5-C6-H6	125.3
C8-H8B	0.9800	Si-C7-H7A	109.5
C8-H8C	0.9800	Si-C7-H7B	109.5
C9-C10	1.440(10)	H7A-C7-H7B	109.5
C9-C11	1.479(17)	Si-C7-H7C	109.5
C10-H10A	0.9800	H7A-C7-H7C	109.5
C10-H10B	0.9800	H7B-C7-H7C	109.5
C10-H10C	0.9800	Si-C8-H8A	109.5
C11-H11A	0.9600	Si-C8-H8B	109.5
C11-H11B	0.9601	H8A-C8-H8B	109.5
C12-C13	1.513(8)	Si-C8-H8C	109.5
C12-C14	1.524(8)	H8A-C8-H8C	109.5
C12-H12	1.0000	H8B-C8-H8C	109.5
C13-H13A	0.9800	C10-C9-C10$^{(i)}$	107.3(15)
C13-H13B	0.9800	C10-C9-C11	106.5(9)
C13-H13C	0.9800	C10-C9-C3	110.9(6)
C14-H14A	0.9800	C11-C9-C3	114.3(8)
C14-H14B	0.9800	C9-C10-H10A	109.5
C14-H14C	0.9800	C9-C10-H10B	109.5
C15-H15A	0.9800	H10A-C10-H10B	109.5
C15-H15B	0.9800	C9-C10-H10C	109.5

H10A-C10-H10C	109.5	H13A-C13-H13C	109.5
H10B-C10-H10C	109.5	H13B-C13-H13C	109.5
C9-C11-H11A	109.6	C12-C14-H14A	109.5
C9-C11-H11B	109.4	C12-C14-H14B	109.5
H11A-C11-H11B	109.5	H14A-C14-H14B	109.5
C13-C12-C5	110.3(5)	C12-C14-H14C	109.5
C13-C12-C14	109.1(4)	H14A-C14-H14C	109.5
C5-C12-C14	112.3(5)	H14B-C14-H14C	109.5
C13-C12-H12	108.4	Ta-C15-H15A	109.5
C5-C12-H12	108.4	Ta-C15-H15B	109.5
C14-C12-H12	108.4	H15A-C15-H15B	109.5
C12-C13-H13A	109.5	Ta-C15-H15C	109.5
C12-C13-H13B	109.5	H15A-C15-H15C	109.5
H13A-C13-H13B	109.5	H15B-C15-H15C	109.5
C12-C13-H13C	109.5		

Symmetry transformations used to generate equivalent atoms:
(i) x,-y+1/2,z

[a] CpA is the centroid of atoms C1, C2, C3, C4 and C5
[b] PlnA is the best plane through atoms C1, C2, C3, C4 and C5
[c] CpB is the centroid of atoms C6, C7, C8, C9 and C10
[d] PlnB is the best plane through atoms C6, C7, C8, C9 and C10

Table S36. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for $[(Me_2Si)_2(\eta^5\text{-}4\text{-}CMe_3\text{-}C_5H_2)(\eta^5\text{-}3,5\text{-}CMe_2H\text{-}C_5H_1)]Ta(CH_2)CH_3$ (24, CCDC 147413).
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ta	79(2)	70(2)	93(2)	0	27(1)	0
Si	96(7)	128(8)	149(9)	48(7)	34(7)	-11(6)
C1	70(30)	150(30)	150(30)	20(30)	60(20)	40(20)
C2	70(30)	80(30)	190(30)	0(20)	50(20)	-10(20)
C3	80(40)	130(40)	150(50)	0	40(40)	0
C4	50(20)	120(30)	80(30)	0(20)	10(20)	-50(20)
C5	70(20)	100(30)	100(30)	-20(20)	-10(20)	10(20)
C6	70(40)	110(40)	130(40)	0	40(30)	0
C7	250(30)	340(40)	190(40)	90(30)	80(30)	-40(30)
C8	150(30)	150(30)	310(40)	60(30)	50(30)	-30(20)
C9	100(40)	240(40)	120(50)	0	-30(40)	0
C10	2220(150)	2260(160)	420(70)	720(90)	-830(90)	-2010(140)
C11	420(80)	3100(300)	140(70)	0	10(70)	0
C12	140(30)	50(20)	200(30)	10(20)	40(30)	20(20)
C13	180(30)	140(30)	240(40)	50(30)	50(30)	40(20)
C14	150(30)	90(30)	280(40)	-30(30)	50(30)	30(20)
C15	180(30)	430(40)	150(40)	-70(30)	0(30)	100(30)

Table S37. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for [$(Me_2Si)_2(\eta^5$-4-CMe_3-$C_5H_2)(\eta^5$-3,5-CMe_2H-C_5H_1)]$Ta(CH_2)CH_3$ (24, CCDC 147413).

	x	y	z	U_{iso}
H2	618	124	-35	13
H6	1299	250	114	12
H7A	749	107	462	31
H7B	829	199	496	31
H7C	950	119	543	31
H8A	756	7	240	25
H8B	958	3	289	25
H8C	841	32	128	25
H10A	273	179	-387	244
H10B	283	178	-224	244
H10C	420	128	-266	244
H11A	460	250	-453	149
H11B	614	201	-341	149
H12	1125	55	153	17
H13A	1350	-1	353	23
H13B	1231	55	407	23
H13C	1410	90	414	23
H14A	1385	27	128	22
H14B	1449	119	180	22
H14C	1293	105	30	22
H15A	806	131	-156	33
H15B	981	102	-32	33
H15C	983	166	-153	33

Principal mean square atomic displacements U

0.0099	0.0078	0.0070	Ta								
0.0204	0.0099	0.0081	Si								
0.0176	0.0138	0.0049	C1								
0.0190	0.0086	0.0057	C2								
0.0149	0.0133	0.0071	C3								
0.0161	0.0089	0.0029	C4								
0.0159	0.0088	0.0050	C5								
0.0129	0.0105	0.0071	C6								
0.0411	0.0235	0.0131	C7								
0.0366	0.0164	0.0102	C8								
0.0235	0.0234	0.0053	C9								
0.5687	0.0333	0.0068	C10	may be split into	0.3326	0.1917	-0.2645	and	0.3674	0.1644	-0.3050
0.3076	0.0509	0.0132	C11	may be split into	0.5439	0.2657	-0.3560	and	0.5439	0.2343	-0.3560
0.0231	0.0139	0.0048	C12								
0.0275	0.0206	0.0102	C13								
0.0323	0.0160	0.0070	C14								
0.0527	0.0177	0.0115	C15								

Least-squares planes (x,y,z in crystal coordinates) and deviations from them
(* indicates atom used to define plane)

8.4712 (0.0053) x + 0.0000 (0.0002) y - 4.6438 (0.0329) z = 5.3534 (0.0052)

* -0.0049 (0.0015) C1
* 0.0128 (0.0038) C2
* -0.0157 (0.0047) C3
* -0.0049 (0.0015) C1_$1
* 0.0128 (0.0038) C2_$1
2.1174 (0.0035) Ta

Rms deviation of fitted atoms = 0.0111

4.0385 (0.0289) x - 0.0000 (0.0002) y + 6.3199 (0.0299) z = 6.0325 (0.0261)

Angle to previous plane (with approximate esd) = 66.99 (0.29)

* -0.0068 (0.0015) C4
* 0.0182 (0.0039) C5
* -0.0227 (0.0049) C6
* -0.0068 (0.0015) C4_$1
* 0.0182 (0.0039) C5_$1
-2.1258 (0.0036) Ta

Rms deviation of fitted atoms = 0.0159